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(54) **Silicon nitride ceramics containing a dispersed pentamolybdenum trisilicide phase.**

(57) A sintered silicon nitride ceramic product that has high strength at both ambient and elevated temperatures, good oxidation resistance at high temperatures and retention of strength after exposure to oxidizing conditions. contains 1 to 80 wt. %  $\text{Mo}_5\text{Si}_3$ .

This invention relates to sintered silicon nitride ceramics.

Silicon nitride is of great interest for structural and electronic applications because of its excellent high temperature strength, good thermal shock resistance, good wear resistance and chemical inertness. Silicon nitride materials have traditionally been fabricated by one of three methods: (1) the direct nitridation of silicon powder at high temperatures, (2) densification of commercially available silicon nitride powder at high temperatures by the addition of metal oxide powders known as sintering aids, and (3) densification of commercially available silicon nitride powder at high temperatures and pressures, a process known as hot pressing. These silicon nitride materials have been used in structural applications such as cutting tools and gas turbines.

Although silicon nitride ceramics having satisfactory mechanical properties at ambient and modestly high temperatures are available, many are not suitable for high temperature applications because their toughness, wear resistance and strength are often degraded at temperatures greater than 1000°C. In the case of cutting tool inserts, wear resistance is a particularly important property. Undesirable phase transformations within the insert and chemical reactivity with the metal being worked on cause a deterioration in properties as the temperature rises at the high feeding and rotating speeds used for milling and turning operations.

Various methods have been proposed for improving the high temperature properties of silicon nitride ceramics. For example, a sintered ceramic product exhibiting high strength, toughness and hardness at elevated temperatures is described in U.S.P. 5,094,986. The product contains high metal content silicides of Fe, Ni or Co uniformly dispersed in a silicon nitride matrix having a high alpha-phase content. Silicon nitride compositions containing MoSi<sub>2</sub> have also been prepared. For example, U.S.P. 3,002,936 discloses a sintered mixture of silicon nitride and MoSi<sub>2</sub> for applications requiring low electrical resistance as well as high thermal shock resistance. However, no compositions have been disclosed that comprise a homogeneous dispersion of a Mo<sub>5</sub>Si<sub>3</sub> phase in a silicon nitride matrix.

The sintered silicon nitride ceramic products of this invention comprising (a) from 20% to 98% silicon nitride and (b) from 0.02% to 20% of at least one oxide, nitride or silicate of an element selected from IUPAC groups 2, 3, 4, 13 or the lanthanide series, all percentages being by weight based on the total weight of the product, are characterized in that they further comprise from 1% to 80% Mo<sub>5</sub>Si<sub>3</sub>.

Also according to this invention, these compositions can be used for making cutting tools.

The products have high strength at both ambient and elevated temperatures, good oxidation resistance at high temperatures and retention of strength after exposure to oxidizing conditions.

Since Mo<sub>5</sub>Si<sub>3</sub> powder is not commercially available at the present time, a preferred method for preparing the sintered ceramic products of this invention comprises (1) intimately mixing a powder mixture of (a) 20% to 98% silicon nitride, (b) 1% to 80% molybdenum metal, or an oxide or alloy thereof, and (c) 0.02% to 20% of at least one oxide, nitride or silicate of an element of IUPAC group 2, 3, 4, 13 or the lanthanide series, all percentages being by weight based on the total weight of the powder mixture, (2) reacting the components of the powder mixture by heating to a temperature of 1300° to 1700°C in a nonoxidizing atmosphere until the molybdenum is completely converted to Mo<sub>5</sub>Si<sub>3</sub> and (3) maintaining the mixture at a temperature of 1300° to 1700°C in the nonoxidizing atmosphere until the composition densifies. A combination of alumina and yttria is the preferred sintering aid. This process is described in more detail in U.S.P. 5,023,214.

The silicon nitride used in the process of this invention can be any commercially available silicon nitride powder. The silicon nitride is used in an amount of 50% to 98%, based on the total weight of the composition.

Other refractory compounds, which can be chemically stable or unstable, can replace up to 50% by weight of the silicon nitride. For example, nitrides such as aluminum nitride, titanium nitride and boron nitride; carbides such as silicon carbide, titanium carbide and boron carbide; and borides such as titanium diboride, molybdenum diboride, and zirconium diboride can be used to replace silicon nitride. The refractory compound can be chosen to enhance a particular property of the resulting composite. For example, including titanium carbide or silicon carbide in the composition will give a harder product.

The silicon nitride powder is mixed with from 1% to 80%, preferably 5% to 25%, based on the total weight of the composition, of molybdenum metal. An oxide or alloy of molybdenum can also be used.

The powder mixture also includes from 0.02% to 20%, preferably from 1% to 10%, based on the total weight of the composition, of a sintering aid. Amounts higher than about 20% degrade the mechanical properties of the sintered product. The sintering aid is an oxide, nitride or silicate of an element of IUPAC groups 2, 3, 4, 13 or the lanthanide series, or mixtures thereof. Oxides of aluminum, magnesium, hafnium, calcium, strontium, zirconium and yttrium are preferred. A combination of aluminum oxide and yttrium oxide is most preferred. The silicate sintering aid can be added as such or can be formed in situ by the reaction

of an oxide or nitride sintering aid with the silica that is always present on the surface of the silicon nitride powder. When a nitride sintering aid is used, it is sometimes desirable to add silica in addition to that which is inherently present on the surface of the silicon nitride. IUPAC group 1 oxides can be substituted for any of the oxide, nitride or silicate sintering aids in an amount of up to 50% by weight.

The powder mixtures of this invention are preferably densified by simultaneously heating and pressing. The preferred processing techniques are therefore hot pressing, hot isostatic pressing and gas pressure sintering. However, cold pressing followed by pressureless sintering will also yield the products of this invention.

The process for preparing the sintered product involves two steps. The powder mixture is first heated to between 1300° to 1700°C and held for a time sufficient to convert the molybdenum, or an oxide or alloy thereof, to  $\text{Mo}_5\text{Si}_3$ . The molybdenum reacts completely with the silicon nitride to form  $\text{Mo}_5\text{Si}_3$  while evolving nitrogen gas. The preferred temperature for the first step is between 1300° to 1500°C, since  $\text{MoSi}_2$  begins to form at around 1700°C. The amount of time necessary to convert molybdenum to  $\text{Mo}_5\text{Si}_3$  depends on the particle size of the powder mixture, the temperature, and the atmosphere. However, times between 30 minutes and two hours are typically used.

The temperature and time at temperature are then chosen so as to densify the  $\text{Mo}_5\text{Si}_3$ -containing product. Temperatures between 1300° to 1900°C can be used. However, the preferred temperature range is from 1500° to 1700°C. If the temperature is too low, densification will be incomplete. If the temperature is too high, the silicon nitride will decompose. The high melting point of  $\text{Mo}_5\text{Si}_3$  (greater than 1900°C) contributes to the high temperature stability of the sintered product. The densification is preferably carried out at a pressure of at least 1000 psi (70 kg/cm<sup>2</sup>), most preferably 2000 to 6000 psi (140 to 420 kg/cm<sup>2</sup>). A nonoxidizing atmosphere such as nitrogen, hydrogen or helium is used to prevent oxidation of the molybdenum and the silicon nitride. A nitrogen atmosphere is preferred. Often both steps of reacting the silicon nitride with the molybdenum and the densification step can occur simultaneously, depending on the melting point of the sintering aid that is selected.

The sintered ceramic product comprises (1) from 20% to 98% silicon nitride, (b) from 1% to 80%  $\text{Mo}_5\text{Si}_3$ , and (c) from 0.02% to 20% of at least one oxide, nitride or silicate of an element selected from IUPAC group 2, 3, 4, 13 or the lanthanide series, all percentages being by weight based on the total weight of the product.

The product is composed of microscopic "islands" of  $\text{Mo}_5\text{Si}_3$  having a particle size of 0.1 to 10.0 microns homogeneously dispersed throughout a silicon nitride matrix. While the exact mechanism is not known, the morphology of the sintered product of this invention is believed to result from a high temperature disproportionation reaction promoted by the sintering aid. The sintering aid performs a dual role: it first provides a liquid phase during heating that acts as a high temperature "solvent" for both the nitride and the molybdenum (or molybdenum oxide or alloy) and then helps in the consolidation of the material via sintering. The X-ray diffraction pattern of the sintered product indicates that the product is a composite of silicon nitride and  $\text{Mo}_5\text{Si}_3$ . There is no free molybdenum metal or molybdenum oxide present.

The sintered ceramic product of this invention has a wide variety of applications in the structural ceramics area. Because the material has a theoretical density of less than 5, it is suitable for uses where a high strength/weight ratio is important. The unique mechanical properties of the product make it especially suited for use in the manufacture of cutting tools. The material can also be used in the manufacture of turbine engines, valve seals, bearings and other parts requiring exceptional wear resistance.

#### Example 1

The following ingredients are milled using a SWECO vibratory mill equipped with silicon nitride grinding media: silicon nitride (163.8 g), molybdenum (20.0 g), yttria (10.8 g), alumina (5.4 g), RHOPLEX® B-60A polyacrylate emulsion supplied by Rohm & Haas Co. as a dispersant (2.0 ml) and water (200 g). The mixture is milled for 16 hours and the resulting slurry is spray dried using a laboratory spray dryer supplied by Yamato Corp.

Bars (2.5" x 0.5", 6.35 x 1.27 cm) are formed by pressing the powder on a Carver uniaxial hydraulic press at 15 Ksi (103 MPa). The bars are placed in a graphite crucible and packed with silicon nitride powder. All samples are pressureless sintered under a nitrogen atmosphere under the conditions indicated in Table I.

Table I

° C/min	Temp. (° C)	Hold (min)	Major Phases	Density (g/cc)
20	1500	180	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>	3.14
20 10	1500 1700	60 120	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub> , MoSi <sub>2</sub>	3.29
20 10	1500 1625	60 120	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>	3.14

## Example 2

The following ingredients are placed into a SWECO mill and milled in 200 ml of water for 16 hours.

5 wt. % Mo (2a)	Silicon nitride Molybdenum powder Yttria Alumina	432.5 g 25.0 g 28.5 g 14.0 g
10 wt. % Mo (2b)	Silicon nitride Molybdenum powder Yttria Alumina	409.5 g 50.0 g 27.0 g 13.5 g
15 wt. % Mo (2c)	Silicon nitride Molybdenum powder Yttria Alumina	387.0 g 75.0 g 25.5 g 12.5 g
5 wt. % Mo + 10 wt. % AlN (2d)	Silicon nitride Molybdenum powder Yttria Alumina Aluminum nitride	382.5 g 25.0 g 28.5 g 14.0 g 50.0 g

The resulting slurries are spray dried as described in Example 1. The powders are hot pressed at 4 Ksi (28 MPa) pressure under nitrogen to form three-inch (7.6 cm) disks under the conditions indicated in Table II.

Table II

Hot Pressing Conditions					
Powder	°C/min	Temp. (°C)	Hold (min)	Density (g/cc)	Major Phases
2a (5% Mo)	10	1500	60	Porous	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2a (5% Mo)	10 10	1500 1550	60 120	3.28	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2a (5% Mo)	10	1700	120	3.48	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2b (10% Mo)	10	1600	120	3.45	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2b (10% Mo)	10	1700	120	3.38	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub> , MoSi <sub>2</sub>
2c (15% Mo)	10	1600	120	3.52	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2c (15% Mo)	10	1700	120	3.55	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2d (5% Mo + AlN)	10	1600	120	3.23	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub>
2d (5% Mo + AlN)	10	1700	120	3.31	Si <sub>3</sub> N <sub>4</sub> , Mo <sub>5</sub> Si <sub>3</sub> , MoSi <sub>2</sub>

## Example 3

The three-inch (7.6 cm) disks prepared from the powder mixtures described in Example 2 are ground to 4 mm thickness and 3 mm flex bars are cut and chamfered. Six flex bars prepared from each powder sample are tested to determine the four-point flexural strength at room temperature. The results given in Table III are an average of the measurements on six flex bars.

Table III

Powder	Hot Pressing Conditions			Room Temp. Flex Strength (MPa)
	°C/min	Temp. (°C)	Hold (min)	
2d (5% Mo + AlN)	10	1600	120	560
2b (10% Mo)	10	1600	120	647
2c (15% Mo)	10	1600	120	413
2c (15% Mo)	10	1700	120	763

Four flex bars prepared from the same three-inch (7.6 cm) disks are heated in air at 1200°C for a period of 100 hours and the amount of oxidation measured as an increase in weight. Oxidation is reported below in terms of the value obtained by dividing the weight increase of the test sample by its surface area. Samples having the best oxidation resistance are those with the lowest values in mg of mass gained per unit surface area. Oxidation values and flexural strengths reported in Table IV are an average of the measurements on four flex bars.

Table IV

Powder	Hot Pressing Conditions					RT Flex MPa After Oxidation
	Wt. %	°C/min	Temp. (°C)	Hold (min)	Oxidation (mg/cm <sup>2</sup> )	
2d (5% Mo + AlN)	5	10	1700	120	4.455	340
2b (10% Mo)	10	10	1600	120	4.193	591
2c (15% Mo)	15	10	1600	120	3.669	382

Strength retention of sample 2b (10% Mo) is 91% compared to the nonoxidized sample in Example 3. Strength retention of sample 2c (15% Mo) is 92% compared to the nonoxidized sample in Example 3. Samples containing the largest amount of silicide exhibit the least weight gain per unit surface area, indicating that larger amounts of silicide impart greater oxidation resistance.

The IUPAC (International Union of Pure and Applied Chemistry) groups 2, 3, 4 and 13 as used in the present invention comprise the following elements:

Group 2: alkaline earth metals; Group 3: Sc, Y, La, Ac; Group 4: Ti, Zr, Hf; Group 13: B, Al, Ga, In, Tl. The lanthanides include lanthanum, La, plus the elements Ce through Lu (58-71) in the Periodic Table of the Elements.

#### Claims

1. A sintered silicon nitride ceramic product comprising (a) from 20% to 98% silicon nitride and (b) from 0.02% to 20% of at least one oxide, nitride or silicate of an element selected from IUPAC groups 2, 3, 4, 13 or the lanthanide series, all percentages being by weight based on the total weight of the product, characterized in that it further comprises from 1% to 80%  $\text{Mo}_5\text{Si}_3$ .
2. The product of claim 1 further characterized by replacing up to 50% by weight of the silicon nitride by at least one refractory carbide, nitride other than silicon nitride, or boride.
3. The product of claim 2 further characterized in that the refractory nitride is aluminum nitride.
4. The product of claim 1 further characterized in that it comprises 50% to 93% by weight of silicon nitride, 5% to 25% by weight of  $\text{Mo}_5\text{Si}_3$ , 1% to 10% by weight of at least one oxide of IUPAC group 3 elements or the lanthanide series, and 1% to 5% by weight of aluminum oxide.
5. The product of claim 4 further characterized by substituting fully stabilized zirconium oxide, partially stabilized zirconium oxide or hafnium oxide for all or part of the oxide of IUPAC group 3 elements or the lanthanide series.
6. The product of claim 1 further characterized in that it comprises 50% to 93% by weight of silicon nitride, 5% to 25% by weight of  $\text{Mo}_5\text{Si}_3$ , 1% to 10% by weight of at least one oxide of IUPAC group 2 elements or the lanthanide series, and 1% to 5% by weight of aluminum oxide.
7. The product of claim 6 further characterized by substituting fully stabilized zirconium oxide, partially stabilized zirconium oxide or hafnium oxide for all or part of the oxide of IUPAC group 2 elements or the lanthanide series.
8. The product of any of the preceding claims further characterized by having a room temperature flexural strength of at least 400 MPa.
9. A cutting tool prepared from the sintered ceramic product of any of the preceding claims.



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 92 10 9273

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 99, no. 12, 1983, Columbus, Ohio, US; abstract no. 92717J, SUMITOMO ELECTRIC INDUSTRIES, LTD.: 'High-strength silicon nitride sinters'	1,8	C04B35/58 C04B35/65
A	* page 359, column 1, line 12; table 1 * & JP-A-58064270 * abstract *	4-7,9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C04B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14 JULY 1992	Examiner HAUCK H.N.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	